

Distortion Isomerism of Cu(II) Chloride Adducts with Bis(2-benzimidazolyl)ethane. Synthesis, Characterization, X-ray Structures and Spectroscopy of Four Different Isomers

Gerard A. van Albada · Ilpo Mutikainen ·
Urho Turpeinen · Jan Reedijk

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Abstract 3D structures and spectroscopic properties are reported of four compounds with the ligand bis(2-benzimidazolyl)ethane (hereafter abbreviated as dbz) attached to CuCl_2 , all having the general formula $[\text{Cu}(\text{dbz})\text{Cl}_2](\text{Hb})_x$, (in which $\text{Hb} = \text{EtOH}$ or MeOH and $x = 1/2$ or 1). The X-ray crystal structure has been solved from these four slightly different compounds, namely: green α - $[\text{CuCl}_2\text{dbz}](\text{C}_2\text{H}_5\text{OH})_{1/2}$ (**1**), the red compound β - $[\text{CuCl}_2\text{dbz}](\text{C}_2\text{H}_5\text{OH})_{1/2}$ (**2**), which both have two slightly different units in the unit cell, the red α - $[\text{CuCl}_2\text{dbz}](\text{CH}_3\text{OH})$ (**3**) and a blue–green compound β - $[\text{CuCl}_2\text{dbz}](\text{CH}_3\text{OH})$ (**4**). The geometry around the Cu(II) anion is distorted tetrahedral for all four compounds, with chromophores consisting of two nitrogen atoms of the bidentate chelating dbz molecule and two chloride anions.

The unit cells of compound **1** and **2** consist of two chemically identical, but crystallographically different units, while compounds **3** and **4** each have only one independent CuCl_2 –(dbz) unit. The major differences are observed in the dihedral angles NCuN–ClCuCl , which vary from 29.3 to 77.1° for the four compounds. The differences are related to different packing effects, ring–ring stacking and H-bond interaction, due to the two different alcohols used. In fact these four compounds represent a new range of examples of distortion isomerism in pseudo-tetrahedrally coordinated species. Characterisation of the four

compounds has been completed by IR, EPR and LF spectroscopy.

Keywords Copper(II) · Plasticity effect · Crystal structure · Distortion isomerism · Hydrogen bonding

Introduction

The coordination chemistry of the heterocyclic azoles acting as ligands in copper(II) compounds in the context of modelling biological systems has gained much interest in the past decades [1–4]. In this respect bis(2-benzimidazoles) have received much attention for their wide-ranging antiviral activity [5, 6], their importance in selective ion-exchange resins [7, 8] and the possibility to form supramolecular aggregates with d^{10} metal ions [9].

So far, spectroscopic and magnetic properties, as well as X-ray structural analysis of a number of mono-, bis-, tetra- and polynuclear copper(II) coordination compounds with bis(2-benzimidazolyl)alkanes and some substituted bis(2-benzimidazolyl)alkanes have been reported by others and by us [10–20].

The copper(II) ion is known to yield in some cases different geometries with the same ligand. This has been coined as “plasticity effect” [21–23] and is believed to result from the Jahn–Teller distortion of the Cu(II) ion. Several ligands are known to yield different (coloured) Cu(II) isomers of the same compound, which have been classified as distortion isomers, a phenomenon known for many years [24–26].

In our earlier research with the ligand bis(2-benzimidazolyl)propane (abbreviated as tbz), two different Cu(II) compounds, of formula $[\text{Cu}(\text{tbz})\text{Cl}_2]$, were obtained, i.e. a red isomer with a (distorted) tetrahedral geometry and a

G. A. van Albada · J. Reedijk (✉)
Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden
University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
e-mail: reedijk@chem.leidenuniv.nl

I. Mutikainen · U. Turpeinen
Laboratory of Inorganic Chemistry, Department of Chemistry,
University of Helsinki, P.O. Box 55, A.I. Virtasenaukio 1, 00014
Helsinki, Finland

Table 1 Crystal and refinement data

Compound	1	2	3	4
CCDC deposit nr.				
Molecular formula	C ₃₄ H ₃₄ Cl ₄ Cu ₂ N ₈ O	C ₃₄ H ₃₄ Cl ₄ Cu ₂ N ₈ O	C ₁₇ H ₁₈ Cl ₂ CuN ₄ O	C ₁₇ H ₁₈ Cl ₂ CuN ₄ O
Molecular weight	839.59	839.59	428.79	428.79
<i>T</i> (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P2(1)/c
<i>a</i> (Å)	12.306(2)	9.2620	8.256(2)	6.994(1)
<i>b</i> (Å)	12.757(2)	12.660(3)	9.082(2)	13.802(3)
<i>c</i> (Å)	13.742(3)	15.457(3)	12.331(2)	18.579(4)
α (°)	67.27(3)	89.55(3)	100.80(3)	90.0
β (°)	63.76(3)	88.44(3)		95.33(3)
γ (°)	84.65(3)	78.72(3)	94.57(3)	90.0
<i>V</i> (Å ³)	1776.9(9)	1776.8(6)	878.0(3)	1785.7(6)
<i>Z</i>	2	2	2	4
<i>F</i> (000)	856	856	438	876
<i>D</i> _{cal} (Mg m ⁻³)	1.569	1.569	1.622	1.595
μ (mm ⁻¹)	1.539	1.539	1.561	1.535
Crystal size (mm)	0.20 × 0.25 × 0.25	0.30 × 0.10 × 0.07	0.20 × 0.20 × 0.04	0.25 × 0.13 × 0.13
Colour, shape	green, block	red, needle	red, plate	bluegreen, block
θ range (°)	2.9–27.5	2.8–27.0	3.16–27.50	2.20–27.55
Number of reflections collected	28,173	28,194	13,257	27,031
Number of unique reflections	8110 (<i>R</i> _{int} = 0.037)	7457 (<i>R</i> _{int} = 0.065)	4010 (<i>R</i> _{int} = 0.083)	4092(<i>R</i> _{int} = 0.1494)
Number of ref. parameters	444	487	228	227
<i>S</i> (Goodness of fit)	0.95	1.048	1.009	0.991
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0294	<i>R</i> 1 = 0.0558	<i>R</i> 1 = 0.0518	<i>R</i> 1 = 0.0686
	<i>wR</i> 2 = 0.0731	<i>wR</i> 2 = 0.1313	<i>wR</i> 2 = 0.1177	<i>wR</i> 2 = 0.1622
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0437	<i>R</i> 1 = 0.0895	<i>R</i> 1 = 0.0901	<i>R</i> 1 = 0.1404
	<i>wR</i> 2 = 0.0749	<i>wR</i> 2 = 0.1488	<i>wR</i> 2 = 0.1310	<i>wR</i> 2 = 0.1940
Largest difference min, max (e Å ⁻³)	−0.59, 0.51	−0.99, 1.04	−0.82, 0.70	−0.58, 1.26

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w\{|F_o| - |F_c|\}^2 / w|F_o|^2]^{1/2}$$

polymeric green isomer containing two different copper(II) sites, each distorted from square planar [14]. With a methyl substituent on different positions on the alkyl chain of tbz a number of copper(II) halide compounds were synthesized, however, no distortion isomers were reported in these cases [19].

In the present study a few other examples dealing with four CuCl₂ distortion isomers are reported with the ligand bis(2-benzimidazolyl)ethane (abbreviated as dbz) having the general formula [Cu(dbz)Cl₂](Hb)_{*x*} (in which Hb = EtOH or MeOH and *x* = 1/2 or 1). The X-ray crystal structure has been solved from four different compounds, the green α -[CuCl₂dbz](C₂H₅OH)_{1/2} (**1**) [27], the red β -[CuCl₂dbz](C₂H₅OH)_{1/2} (**2**), the red α -[CuCl₂dbz](CH₃OH) (**3**) and the blue–green compound β -[CuCl₂dbz](CH₃OH) (**4**). The characterization was further done by spectroscopic methods and EPR. This study is a rare case of distortion isomerism in which four

different CuCl₂ compounds with the same ligand is fully characterized, also by X-ray crystallography.

Experimental section

General

C, H, N determinations were performed on a Perkin Elmer 2400 Series II analyzer. Ligand field spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer, using the diffuse reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH (*g* = 2.0036) as a standard. FTIR spectra were obtained on a Perkin Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4,000–300 cm⁻¹, res. 4 cm⁻¹).

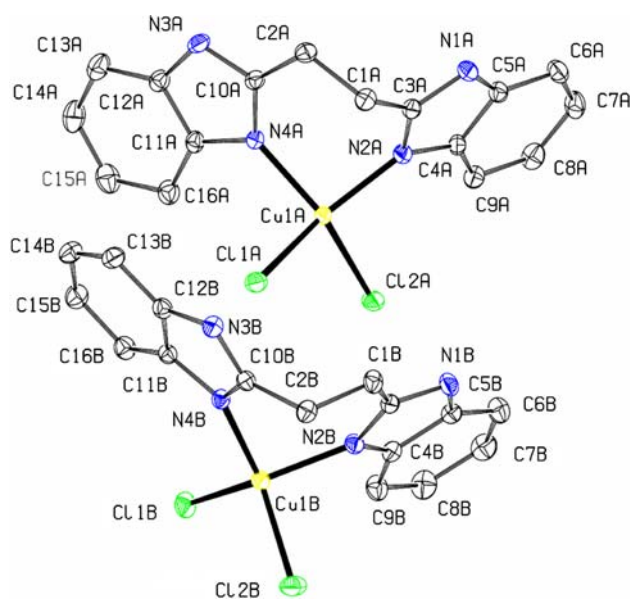


Fig. 1 Thermal ellipsoid plot drawn at the 50% probability level, of compound **1** with atom-labeling scheme. Hydrogen atoms and the non-coordinating ethanol molecule has been omitted for clarity

Synthesis of the coordination compounds

The compounds were prepared according to the following general procedure: 1.2 mmol of CuCl_2 and 1.2 mmol of the ligand dbz were each dissolved in 10 ml of methanol or ethanol. The Cu(II) salt solution was then added slowly to

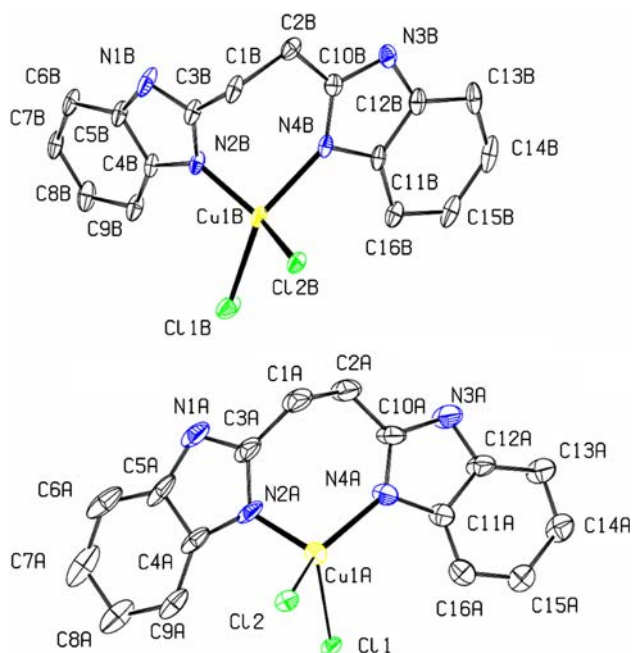


Fig. 2 Thermal ellipsoid plot drawn at the 50% probability level, of compound **2** with atom-labeling scheme. Hydrogen atoms and the non-coordinating ethanol molecule has been omitted for clarity. Only one modification of the disordered Cl atoms (attached to Cu1A) are shown

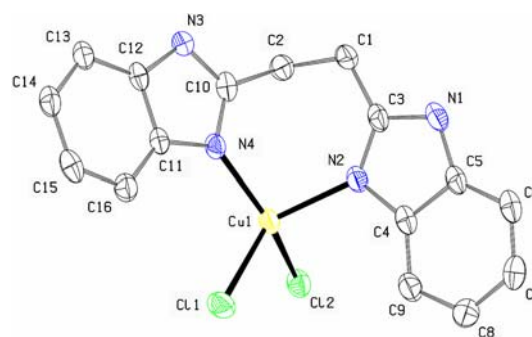


Fig. 3 Thermal ellipsoid plot drawn at the 50% probability level, of compound **3** with atom-labeling scheme. Hydrogen atoms and the non-coordinating methanol molecule has been omitted for clarity

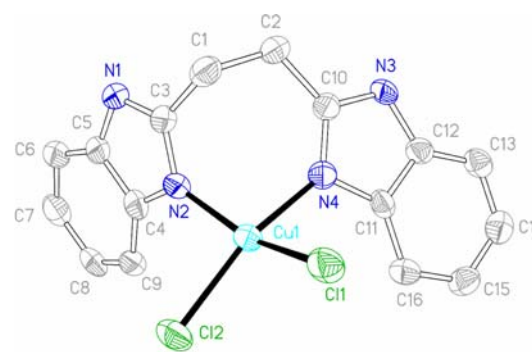


Fig. 4 Thermal ellipsoid plot drawn at the 50% probability level, of compound **4** with atom-labeling scheme. Hydrogen atoms and the non-coordinating methanol molecule has been omitted for clarity

the ligand solution and filtered to remove any undissolved material. Usually after a few days the products separated as a mixture of red and green crystals for the ethanol solution or red and blue–green crystals for the methanol solution. The different coloured crystals were separated manually for spectroscopic measurements and X-ray crystallography.

Changing the Cu/ligand ratio appeared to have a small effect on the crystallisation of the different coloured products, but it was not possible to synthesize these isomers completely separately. Satisfactory elemental (C, H, N) analysis were obtained.

Crystal structure determination and refinement

A crystal was selected and mounted to a glass fiber using the oil-drop method; data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated Mo- $K\alpha$ radiation). The intensity data were corrected for Lorentz and polarization effects, for absorption and for extinction. The structures were solved by direct methods. The programs COLLECT [28], SHELXS-97 [29], SHELXL-97 [30] were used for data reduction, structure solution and structure refinement, respectively. Refinement of F^2

Table 2 Selected bond lengths (Å) and angles (°) for the four compounds

Compound	(1)	(2)	(3)	(4)
Cu1A–Cl1A	2.2664(7)	2.304(3)*	2.265(1)	2.279(2)
Cu1A–Cl1		2.402(2)*		
Cu1A–Cl2A	2.2367(8)	2.152(3)*	2.255(1)	2.234(2)
Cu1A–Cl2		2.319(3)*		
Cu1A–N2A	1.988(2)	1.801(5)	2.013(3)	1.996(5)
Cu1A–N4A	2.004(2)	2.116(5)	1.976(3)	2.007(4)
Cu1B–Cl1B	2.2724(9)	2.356(2)		
Cu1B–Cl2B	2.2371(8)	2.208(1)		
Cu1B–N2B	1.9765(17)	1.843(3)		
Cu1B–N4B	1.973(2)	2.141(4)		
Cl1A–Cu1A–Cl2A	95.62(4)	104.8(1)*	94.17(4)	94.11(6)
Cl1–Cu1A–Cl2		95.43(9)*		
Cl1A–Cu1A–N2A	148.80(7)	109.2(2)*	128.9(1)	156.8(1)
Cl1–Cu1A–N2A		112.4(2)*		
Cl1A–Cu1A–N4A	91.21(6)	128.3(1)*	100.48(9)	90.5(1)
Cl1–Cu1A–N4A		104.4(1)*		
Cl2A–Cu1A–N2A	94.22(6)	116.1(2)*	96.9(1)	93.7(1)
Cl2–Cu1A–N2A		105.7(2)*		
Cl2A–Cu1A–N4A	151.33(7)	99.1(2)*	146.38(9)	161.3(1)
Cl2–Cu1A–N4A		138.6(2)*		
N2A–Cu1A–N4A	94.17(8)	99.8(2)	97.1(1)	89.1(2)
Cl2B–Cu1B–N4B	140.55(7)	98.2(1)		
N2B–Cu1B–N4B	94.68(8)	90.9(2)		
Cl1B–Cu1B–N4B	103.32(7)	140.0(1)		
Cl1B–Cu1B–Cl2B	98.64(4)	95.53(6)		
Cl1B–Cu1B–N2B	132.13(7)	103.4(1)		
Cl2B–Cu1B–N2B	94.33(7)	137.8(1)		
Hydrogen bonds:				
	D–H	H...A	D...A	D–H...A
Structure (1):				
O1–H1A...Cl1B [–1–x, –y, –z]	0.84	2.31	3.146(2)	173
N1A–H1AA...Cl2B [x, 1 + y, –1 + z]	0.88	2.28	3.147(2)	169
N3A–H3AA...Cl1A [–1–x, 1–y, –1–z]	0.88	2.56	3.248(2)	136**
N3A–H3AA...O1 [–1–x, 1–y, –1–z]	0.88	2.43	3.131(3)	138**
N1B–H1BA...Cl2A [1 + x, y, z]	0.88	2.54	3.262(2)	140
N3B–H3BA...O1 [1 + x, y, z]	0.88	1.98	2.830(3)	162
Structure (2):				
*O1–H1A...N1B [1–x, 1–y, 1–z]	0.84	2.28	2.778(9)	119
N1A–H1AC...Cl1B	0.88	2.43	3.210(5)	148
N3A–H3AA...O3 [x, 1 + y, z]	0.88	2.05	2.917(11)	167
N1B–H1BC...O1 [1–x, 1–y, 1–z]	0.88	1.95	2.778(9)	156
N3B–H3BA...Cl2B [1–x, 2–y, 1–z]	0.88	2.61	3.369(4)	145
Structure (3):				
O16–H16A...Cl1 [1–x, 1–y, 1–z]	0.84	2.37	3.175(3)	160
N1–H1C...O16	0.88	2.03	2.853(5)	154
N3–H3A...Cl2 [1 + x, y, z]	0.88	2.60	3.406(4)	153
Structure (4):				
N(1)–H(1A)...O(18) [1–x, 2–y, 1–z]	0.88	1.98	2.776(7)	150

Table 2 continued

Compound	(1)	(2)	(3)	(4)
N(3)–H(3A)···Cl(1) [1–x, 2–y, 1–z]	0.88	2.50	3.257(4)	144
O(18)–H(18A)···Cl(2) [x, 5/2–y, 1/2 + z]	0.84	2.66	3.499(6)	174

* disordered atom

** bifurcated H-bond

was done against all reflections. All non-hydrogen atoms were refined anisotropically. The ethanol molecule and the Cl atoms coordinated to the Cu1A atom in compound **(2)** were found in disordered positions. These disordered atoms were refined in the two positions with population parameter 0.5. All H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Crystallographic data are presented in Table 1

Results and discussion

Description of the crystal structures

A thermal ellipsoid plot, together with the numbering scheme for the four compounds is shown in Figs. 1–4, for compounds **1** to **4**, respectively. The selected bond lengths and bond angles are given in Table 2.

The structure of compounds **1** and **2** contains two chemically almost identical, but crystallographically independent, CuCl₂-dbz units and one non-coordinating ethanol molecule, which is present in a disordered position for compound **2**. In compound **2** also one of the two units contains the two chloride atoms in disordered positions, which appears to be related to the hydrogen-bonding interaction with the disordered ethanol. Compounds **3** and **4** have only one crystallographic unit and one non-coordinating methanol molecule.

Each copper(II) atom is tetrahedrally surrounded by two nitrogens of the chelating bidentate ligand and two chloride anions. The Cu–N distances vary from 1.801(5) to 2.141(4) Å and the Cu–Cl distances vary from 2.152(3) to 2.279(2) Å (the disordered Cu–Cl distances are not considered), which are normal distances for CuCl₂ tetrahedral compounds. The smallest tetrahedral angles (N–Cu–N) of the 7-membered chelate ring differs from 89.12(18)° to 99.8(2)° in the four compounds. Structural comparison of the four compounds is given in Table 3. The fact that in compound **2** the Cl atoms in one of the units is disordered makes it somewhat difficult to compare these compounds with each other.

One of the important differences is the dihedral angle between the Cl–Cu–Cl and the N–Cu–N planes in the four compounds (see Table 3). These tetrahedral angles

differ significantly from the tetrahedral angles reported for the copper(II) halide compounds with tbz and methylated tbz (dihedral angles 62.52 and 65.43°); values of 90° would be expected for undistorted tetrahedral geometry, so the present compounds are more close to tetrahedral than the tbz or methylated tbz compounds, perhaps also influenced by the fact that tbz and methylated tbz compounds forms an eight-membered chelate ring [19], while the present compounds forms a seven-membered chelate ring.

The lattice structure is additionally stabilized by stacking between the benzimidazole groups of different units (Ring–Ring distances are 3.552, 3.416, 3.500, 3.451 Å, for compounds **1** to **4**, respectively). An extensive hydrogen bond system is present between the N–H of the ligand and the chloride ions; between the N–H and the oxygen atom of the alcohol molecule and between the oxygen atom of the alcohol molecule and the chloride ions. Details of the H bonds are given in Table 2. This great variety in H bonds is likely to be responsible for the different distortion isomers found.

Ligand field and infrared spectroscopy

The diffuse reflectance spectra of the powdered solids are given in Table 4, together with the EPR values. The compounds **1** to **3** show the typical tetrahedral-type ligand field spectrum of a very broad (split) band with a centre around $12.0\text{--}9.7 \times 10^3 \text{ cm}^{-1}$, whereas compound **4** has a very broad band centred around $15.0 \times 10^3 \text{ cm}^{-1}$, which are known to be in the common range of absorptions for (square-planar distorted) tetrahedral copper(II) compounds [14, 19, 31].

The infrared spectra of the four compounds show only some differences in the characteristic benzimidazole C–H bending vibrations in the 700–800 cm^{−1} area. The benzimidazole–CH bending vibrations between 750–720 cm^{−1} are known to be very sensitive to structure differences and orientations of the benzene part of the molecule in the lattice [32]. In the dbz free ligand the imidazole bending vibration is observed at 775 cm^{−1} and the benzimidazole CH-out-of-plane bending at 750 and 739 cm^{−1} [32a].

These infrared vibrations in compound **1** are observed at 761, 753, 750, 744 and 736 cm^{−1}; the two red compounds,

Table 3 Structural comparison of the four distortion isomers

Compound	Colour	Cu–N dist. (Å)	Cu–Cl dist. (Å)	Cl–Cu–Cl angle (°)	N–Cu–N angle (°)	Dihedral angle (°)
1. α -[CuCl ₂ dbz] ₂ (C ₂ H ₅ OH) *	green	1.973(2)–2.004(2)	2.2367(8)–2.2724(9)	95.62(4) 98.64(4)	94.17(8) 94.68(8)	41.01(9) 59.47 (9)
2. β -[CuCl ₂ dbz] ₂ (C ₂ H ₅ OH) *	red	1.801(5)–2.141(4)	2.152(3)–2.402(2)**	95.43(9) / 104.8(1) **	99.8(2) 90.9(2)	76.6(3)/77.1(2) 57.6(2)
3. α -[CuCl ₂ dbz](CH ₃ OH)	red	1.976(3)–2.013(3)	2.2550(1)–2.265(1)	94.17(4)	97.1(1)	59.5(1)
4. β -[CuCl ₂ dbz](CH ₃ OH)	Blue–green	1.996(5)–2.007(4)	2.234(2)–2.279(2)	94.11(6)	89.1(2)	29.3(2)

* two crystallographic independent Cu units present in the unit cell

** disordered Cl atoms in one of the two crystallographic independent Cu units

2 and **3** have almost the same pattern, bands at 761, 753, 746, 733 cm^{−1} (compound **2**) and 762, 753, 747, 733 cm^{−1} (for compound **3**). The blue–green compound **4** has a pattern of three vibrations at 764, 757 and 752 cm^{−1}. The ligand N–H stretches vary for each of the compounds (3,464–3,000 cm^{−1}), which is related to their hydrogen bonding situation [34]. The bands are, however, too broad to allow a study with comparison of H-bond distances, also because of the lattice EtOH and MeOH OH-stretching vibrations, which occur in the same region.

EPR

X-band EPR spectra of polycrystalline powders of the complexes were recorded at room temperature and 77 K. The resolution did not improve very much upon cooling to 77 K. As shown in Table 2 the compounds show an axial $S = 1/2$ signal with a g_{\perp} at 2.11–2.07 and an unresolved g_{\parallel} value in the range of 2.23–2.32. EPR measurements as frozen solutions (DMSO/MeOH mixtures) resulted in resolved spectra with g_{\perp} of 2.07, g_{\parallel} 2.32 and A_{\parallel} between 12.7–14.4. These values differ from the earlier reported CuCl₂-(tbz) compounds which show in similar solutions solution a trigonal-bipyramidal geometry; perhaps some dmso is coordinating to the metal of the CuCl₂-(tbz), thereby changing the spectral parameters [14]. The g values obtained are nevertheless in the usual range for copper in a (distorted) tetrahedral environment [14, 16, 19, 21].

Conclusion

The present study has provided four new samples of Cu(II) distortion isomeric compounds with the ligand dbz. So far only a few examples of CuCl₂-based distortion isomers are known which have been fully characterized by X-ray analysis [14, 26d, h], and the present species are the first examples in which four different compounds of the same ligand and metal salt and the same chromophore are fully characterized by X-ray crystallography. All compounds exhibit a more or less distorted tetrahedral environment and a seven-membered chelate ring is formed. The tetrahedral angles (N–Cu–N) of the chelate rings are close to the calculated value (101.3°) for 7-membered chelate rings [33].

The difference in the dihedral angles for the various isomers can be understood on the basis of different hydrogen bonding due to the fact of two different solvents and differences in packing due to ring–ring stacking, thereby illustrating that the energy differences are small. Another interesting fact is that in compound (2) the

Table 4 Ligand field/EPR of the four Cu distortion isomeric

Compound	Colour	LF ($\times 10^3 \text{ cm}^{-1}$) ^a	EPR solid, RT		EPR (frozen. sol) 77 K ^b		
			g_{\perp}	g_{\parallel}	g_{\perp}	g_{\parallel}	A_{\parallel}
1. α -[CuCl ₂ dbz] ₂ (C ₂ H ₅ OH)	green	9.7 (br,sh) 12.1	2.08	2.29	2.07	2.32	13.9
2. β -[CuCl ₂ dbz] ₂ (C ₂ H ₅ OH)	red	9.7 (vbr)	2.11	2.32	2.07	2.32	14.4
3. α -[CuCl ₂ dbz](CH ₃ OH)	red	9.5 (br)	2.09	2.30	2.07	2.32	13.7
4. β -[CuCl ₂ dbz](CH ₃ OH)	blue-green	11.1(sh) 15.0 (vbr)	2.07	2.23	2.07	2.32	14.1

^a abbreviations: vbr = very broad, br = broad, sh = shoulder^b frozen solution mixture DMSO/Methanol 1:1; A_{\parallel} in mT

chloride anions are disordered, the reason for that is still unknown.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC: 602249, 602250, 602251 and 602252, for compounds **1** to **4**, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:int code +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk).

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